Bioresource Technology 123 (2012) 338–343

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Measuring the concentration of carboxylic acid groups in torrefied spruce wood

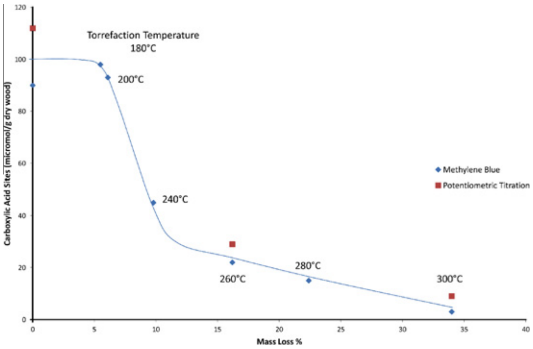
Tooran Khazraie Shoulaifar *, Nikolai DeMartini, Ari Ivaska, Pedro Fardim, Mikko Hupa

Åbo Akademi University, Process Chemistry Center, Piispankatu 8, FI-20500 Turku, Finland

HIGHLIGHTS

- ▶ Methylene blue sorption and titration were used to quantify the carboxylic groups.
- ▶ More than 50% of the carboxylic acid sites decomposed during 30 min. at 240 °C.
- ▶ The change in carboxylic acid content agrees with moisture content results.
- ▶ These methods can be used to help choose torrefaction conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 May 2012
Received in revised form 17 July 2012
Accepted 19 July 2012
Available online 27 July 2012

Keywords:
Torrefaction
Spruce wood
Carboxylic acid groups
Potentiometric titration
Methylene blue sorption

ABSTRACT

Torrefaction is moderate thermal treatment (~200–300 °C) to improve the energy density, handling and storage properties of biomass fuels. In biomass, carboxylic sites are partially responsible for its hygroscopic. These sites are degraded to varying extents during torrefaction. In this paper, we apply methylene blue sorption and potentiometric titration to measure the concentration of carboxylic acid groups in spruce wood torrefied for 30 min at temperatures between 180 and 300 °C. The results from both methods were applicable and the values agreed well. A decrease in the equilibrium moisture content at different humidity was also measured for the torrefied wood samples, which is in good agreement with the decrease in carboxylic acid sites. Thus both methods offer a means of directly measuring the decomposition of carboxylic groups in biomass during torrefaction as a valuable parameter in evaluating the extent of torrefaction which provides new information to the chemical changes occurring during torrefaction.

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1. Introduction

Torrefaction has been defined as a mild heating of biomass under atmospheric conditions in the absence of oxygen at moderate temperature (200–300 °C) (Bergman and Kiel, 2005); though a number of experiments in this temperature range have been carried out in water vapor or air (Acharjee et al., 2011; Almeida et al., 2010). Torrefaction yields a solid fuel that is more easily grindable (Arias et al., 2008), with a higher energy density (Bergman and Kiel, 2005), and with a lower moisture content and reduced hygroscopic nature (Acharjee et al., 2011; Almeida et al., 2009), which reduces the susceptibility of the biomass to biological decay (Kamdem et al., 2000).

The mass loss of torrefaction is a mix of evaporation and decomposition of the biomass components. After evaporation of the water in the biomass, extractives start to degrade (Raveendran et al., 1996). At about 200 °C, hemicellulose and lignin start to degrade but only to a small extent (Raveendran et al., 1996; Chen and Kuo, 2011; Shafizadeh and McGinnis, 1971; Yang et al., 2007). The extent of hemicellulose degradation increases significantly at about 250 °C. Cellulose degradation has been shown to be severe already at 290 °C (Chen and Kuo, 2011). During torrefaction, there is a slight decrease in the O/C ratio (Bridgeman et al., 2008; Van der

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* Corresponding author.
E-mail address: tkhazrai@abo.fi (T. Khazraie Shoulaifar).

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http://dx.doi.org/10.1016/j.biortech.2012.07.069

Stelt et al., 2011) and an increase in the heating value of the resulting torrefied biomass. The increased heating value coupled with a decrease in the mass results in a higher energy density.

There are different types of acids in wood, including carboxylic acids with pK_a of 3.5–4, fatty and resin acids with pK_a = 5–6.5, phenolic groups in lignin with p$K \approx 10$ as very weak acids, and aliphatic hydroxyl groups which are even weaker with p$K > 12$ (Holmbom et al., 1998). The carboxylic groups exist primarily in uronic acids in hemicelluloses. It is the degradation of carboxylic acids that we are measuring in this work.

Acid–base titrations as well as different sorption and ion-exchange techniques have been compared for measuring the concentration of carboxylic acid sites in pulp samples (Fardim et al., 2002). Both methylene blue sorption and potentiometric titration were found to give similar results. In this study, methylene blue sorption and potentiometric titration are used as two methods to measure the concentration of carboxylic acid sites in the original wood and torrefied wood samples.

Methylene blue sorption is a dye adsorption technique, in which the cation part of methylene blue binds with anionic carboxylic groups (Davidson, 1947) as expressed by the reaction:

$$\mathrm{R-COO^-} + \mathrm{Mb^+} \leftrightarrow \mathrm{R-COOMb} \tag{1.1}$$

in which, R–COO$^-$ represents the carboxylic groups and Mb$^+$ represents the methylene blue cations in the dye solution. In methylene blue sorption, the solution is buffered to a pH of 7.8–8.0. At this pH the carboxylic acids with a pK_a lower than ~7.8 will be primarily in their anionic form. This pH also allows for better sorption (Davidson, 1947). This method has been applied to measuring the concentration of acid groups in pulp (Fardim and Holmbom, 2003), wood (DeGroot, 1985; Werkelin et al., 2010), other biomass samples such as Carica papaya seeds (Unuabonah et al., 2009); and coal (Schafer, 1979).

Potentiometric titration is an acid–base titration technique in which acidic groups in the sample are titrated with a base. In this technique, strong acid is first added to make sure all acidic groups are protonated, and then the solution is titrated with a strong base in a nitrogen atmosphere. This method has been applied previously to pulp (Karhu, 2008; Laine et al., 1994; Su et al., 2010) and been found to give similar results to methylene blue titration (Fardim et al., 2002).

In this work, the change in the concentration of the carboxylic acid groups have been determined with both methylene blue sorption and potentiometric titration after torrefaction for 30 min at temperatures of 180, 200, 220, 240, 260, or 300 °C. In addition, the equilibrium moisture content of the torrefied samples has been determined. The hygroscopic nature of biomass is due in part to the carboxylic acid groups, and thus, is an indirect measure of their decomposition. The objective of this study is to measure the concentration of carboxylic groups in torrefied spruce wood, a key reaction in torrefaction. This will provide a tool to measure the extent of a key reaction in torrefaction.

2. Methods

2.1. Samples

The Spruce wood sample was the same wood sample studied in an earlier work (Werkelin et al., 2011) and subsequently had been stored dry. For this project, the wood was ground and sieved to a size of 125–250 μm and then dried at 105 °C for 24 h to ensure it was completely dry before torrefaction. This wood was then split into two parts. Part of the wood was torrefied without any additional pretreatment. Another part of the sample was treated to remove extractives and metals before torrefaction. For removal of the extractives, the wood was first washed with acetone in a Soxhlet apparatus for 6 h at 60 °C and then washed with distilled water for 1 h. Mass loss during acetone extraction was 4.0 wt.% on a dry mass basis. After removal of the extractives, the wood was added to a solution with sodium EDTA and HCl (both 0.01 M) for 2 h to remove and chelate metals. The acid, EDTA and metals were washed away with ultrapure water. The acid-washed wood was then oven dried at 105 °C for 24 h. Both the original wood and acid washed wood were analyzed by ICP-OES (Inductivity Coupled Plasma Spectrometers), Table 1.

2.2. Torrefaction

Torrefaction of the samples was performed in a quartz glass furnace in an electrically heated oven as described elsewhere (DeMartini et al., 2010). Samples of 80 ± 5 mg were placed in a quartz sample holder 15 mm in diameter. Before insertion, the samples were held in an unheated nitrogen purged zone while the oxygen concentration in the reactor dropped to zero. The sample was then inserted into the reactor, which had nitrogen flowing through to remove the torrefaction products and to ensure that the process has been carried out in an oxygen-free environment. The samples were kept in the reactor for 30 min at 180, 200, 240, 260, 280 or 300 °C. The temperature profiles versus time for the biomass sample during torrefaction experiments at 180 and 300 °C are shown in Fig. 1. Based on thermocouple measurements in which the tip of the type K, 0.5 mm thermocouple was placed in the center of the wood sample, it took approximately 5 min to reach the reactor temperature at both 180 and 300 °C. The initial and the final mass of the samples were recorded to determine the mass loss. Multiple torrefaction runs were made at each condition to provide enough samples for the methylene blue sorption and potentiometric measurements. Torrefied samples were kept in desiccators before analysis by methylene blue sorption or potentiometric titration.

2.3. Methylene blue sorption

Methylene blue sorption measurements were carried out with 50 mg of dry sample. Eight samples were analyzed for each condition. The dry wood was mixed with 3 ml of deionized water for 1 h. Then a 0.4 mM MB solution with 0.6 mM barbital to buffer the pH to 7.8–8 was added to the suspensions and mixed for 20 min. This time was studied and found to be sufficient for pulps (Fardim and Holmbom, 2003). The quantity of methylene blue was controlled by adding different volumes of the buffered 0.4 mM methylene blue to each of the eight different solutions containing 50 mg of dry sample each. This gave different methylene blue to wood ratios in each of the eight samples. After 20 min of stirring at room tem-

Table 1
Concentration of inorganics in the original spruce wood and in the acid washed spruce wood. The values for the original wood sample were taken from Werkelin et al. (2010).

Element	Spruce wood (μmol/g wood)	Acid washed wood (μmol/g wood)
K	5.5	n.d.
Na	0.3	n.d.
Ca	18.1	0.9
Mg	3.9	n.d.
Mn	1.8	n.d.
Si	2.1	n.d.
Al	0.1	n.d.
Fe	0.1	n.d.
Cl	1.4	n.d.
S	1.6	n.d.
P	0.1	n.d.

n.d. Not detected.

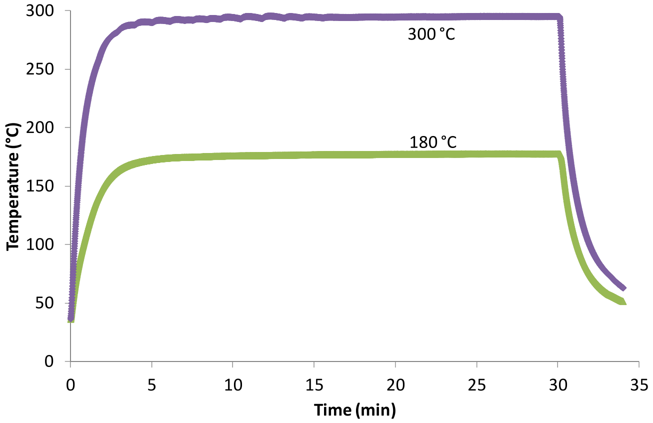

Fig. 1. Time – Temperature history of the sample in the reactor.

perature, the suspensions were filtered through a glass filter. The filtrate was then diluted 25 times using a 0.6 mM barbital solution. The diluted solution was analyzed by UV–Vis spectrophotometry at a wavelength of 664 nm. These results then provided a sorption diagram which was used to determine the total content of acid sites in the wood with a $pK_a < 7.8$. Two blank tests were done to measure the amount of methylene blue that is absorbed to the glass filter and wall. To ensure the repeatability of the methylene blue results, the test was repeated three times for torrefied wood at 260 °C with 22, 22, and 23 μmol/g being obtained for the three analyses.

2.4. Potentiometric titration

For the titrations, 1.5 g of dry accurately-weighed sample was added to 150 ml of 0.1 M $NaNO_3$ solution in a glove box purged with N_2. The $NaNO_3$ solution was prepared fresh for each test from ultrapure water which was boiled to release dissolved CO_2 gas and after that was cooled down in the glove box before the salt was added. The solution was acidified with 1.5 ml of 0.5 M HNO_3 (resulting in a pH of 2) to protonate the acid groups. The solution was then titrated with 0.1 M NaOH using an automatic Metrohm Tiamo titrator. The potential stability criterion (signal drift) in the automatic titration was 0.1 mV min^{-1} with a maximum waiting time of 10 min between dosages. A blank titration test was performed first, in which 1.5 ml of HNO_3 was added to 150 ml, 0.1 M $NaNO_3$ and was titrated with the base until $pH \approx 11$. The difference in the inflection point of the blank titration curve and the inflection point for the titration of the solution containing sample was considered to be the concentration of carboxylic acid groups. Because the inflection point may also be somewhat affected by phenolic groups as well as carboxylic acids, this approach is not fully exclusive only for carboxylic acid sites.

The base used for titration was prepared from Merck, titrisol 1 M NaOH, which was diluted to 0.1 M using ultra pure degassed water. The exact concentration of the NaOH solution was determined by titration of potassium hydrogen phthalate (Harris, 1995). Sodium nitrate was added to the solution of NaOH so that its concentration was 0.1 M. This is done to maintain the ionic strength of the solution containing the wood while it is being titrated.

Titration of the wood in triplicate showed good repeatability, giving values of 80, 93, and 86 μmol/g dry wood. However, for the torrefied samples of the untreated wood at 260 °C and above, the titration curve actually moves to the left of the blank. This is likely due to the presences alkaline and alkaline earth salts in the torrefied wood. When the HNO_3 was added to the sample solution prior to titration, these alkaline salts consumed some of the acid, thereby shifting the inflection point to the left of the blank. Therefore, to obtain the concentration of carboxylic acid sites for the torrefied wood samples, it was necessary to acid wash the chars from torrefaction prior to titration to remove the metals and protonate the acid groups.

2.5. Equilibrium moisture content

The humidity absorption study was conducted by the static desiccator method (Mehta and Singh, 2006). The humidity of the desiccator is maintained by saturated salt solutions (Greenspan, 1977). Different relative humidity levels from 11% to 98% were used. Excess salt was added to the sealed box to ensure that the humidity was constant. The temperature was room temperature, 23 °C. Samples sizes of 90 ± 10 mg, were put in small containers in sealed boxes that contained the saturated salt solutions to give different humidity in the boxes. The samples were then weighed at intervals over 2 weeks. No additional weight gain was observed between day 7 and day 14 and this was taken to be the equilibrium moisture content.

3. Results and discussion

3.1. Mass loss

The mass loss increased with increasing torrefaction temperature from 5.5% ± 0.3% at 180 °C to 34.1 ± 1.1% at 300 °C for untreated wood. These values are consistent with the recorded values for Maritime Pine wood, another type of softwood, ranging from 5.5% at 220 °C (reaction time: 1 h) to 33.3% at 280 °C (reaction time: 5 h) (Pierre et al., 2011). Torrefaction of acid washed wood was carried out at 260 and 300 °C, giving mass losses of 12.9 ± 1.4% and 31.0 ± 1.5%, respectively. The mass loss of the acid-washed wood is less than that of the untreated wood. The difference in the percentage of mass loss between the untreated and acid washed wood can be explained by the 4 wt.% mass loss during acetone extraction. This mass would likely have otherwise been lost during torrefaction at 260 and 300 °C. If this mass loss is considered when calculating the total mass loss for the acid washed wood at 260 and 300 °C, the percentage is similar for both cases.

3.2. Methylene blue sorption

The methylene blue sorption isotherms were used to determine the concentration of carboxylic acid groups in the wood and torrefied wood samples. In the buffered solutions, carboxylic groups with a pK_a less than about 7.8 are predominantly dissociated and thus, they are in their anionic forms and the methylene blue cations can bind to the carboxylic anions. As methylene blue solution is added to the solution containing the sample, the methylene blue binds to the carboxylate ion sites until the sites are saturated, Fig. 2. The adsorption increases up to the saturation point, beyond this point, the further addition of methylene blue results in no additional methylene blue sorption as seen in the plateau in the amount of methylene blue sorbed. This amount in untreated wood was measured to be 90 μmol/g, which is consistent with the values from methylene blue sorption of 86 ± 7 μmol/g reported by Werkelin et al. (2010) for the same wood sample; 81 μmol/g recorded by DeGroot (1985) for cottonwood, and 92 ± 1 μmol/g reported by Fardim et al. (2002) for unbleached spruce thermo-mechanical pulp. After torrefaction of the sample at 180 °C the measured concentration of anionic sites was 98 μmol/g torrefied wood while at 200 °C the concentration was 93 μmol/g torrefied wood. Schafer (1979) measured a slight increase in the concentration of carbox-

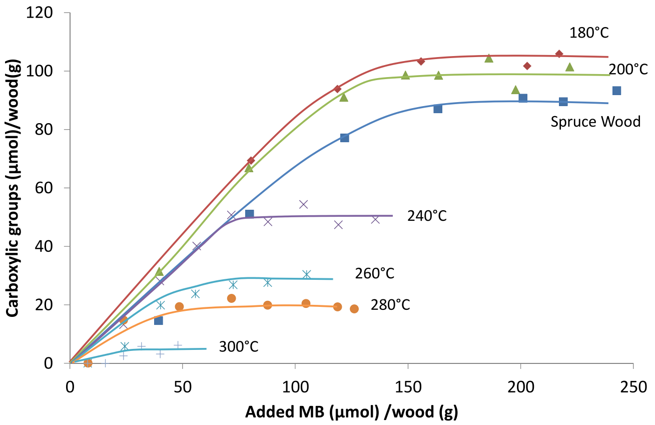

Fig. 2. The concentration of the carboxylic groups for wood and wood torrefied at different temperatures as determined by methylene blue sorption.

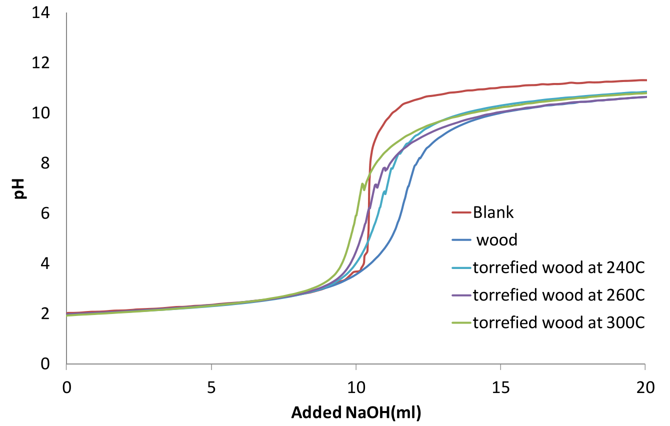

Fig. 3. Potentiometric titration curve of blank, untreated wood and torrefied untreated wood at different temperatures. Biomass sample was 1.500 g suspended in 150 ml of solution. The curves are for samples that have not been acid washed.

ylic acid sites in coal when heat treated to temperatures of 150 and 200 °C. At 240 °C, we measured a 50% reduction in the concentration of carboxylic acid sites and the concentration gradually decreases to 22 µmol/g and 3 µmol/g at 260 °C and 300 °C, respectively. This decrease, to a great extent, is consistent with Schafer (1979) for heat treated coal. At temperatures higher than 250 °C, Rutherford et al. (2008) also found a decrease in the concentration of carboxylic acid sites for heat treated pine wood.

The carboxylic acid concentration measured by methylene blue sorption and the mass loss are given in Table 2. The concentration of carboxylic acid groups in acid washed wood was a little over 10% higher than the untreated wood. For instance, the concentration of non-torrefied acid-washed wood was 103 µmol/g while it was 18 µmol/g at 260 °C and 7 µmol/g at 300 °C. DeGroot (1985) found an increase in the concentration of carboxylic acid sites from 81 to 87 µmol/g when comparing wood with acid washed wood. Methylene blue sorption was similar for both the untreated spruce wood and acid washed spruce wood torrefied at 260 or 300 °C, indicating the carboxylic acid sites of these two samples decomposed similarly when torrefied at these temperatures. The cause for these additional acid sites in the acid treated wood compared to the untreated wood is not fully clear. The removal of extractives, which reduces the mass by about 4%, would only accounts for about 30% of the increased concentration, indicating there may be some additional sites formed during acid washing. The reason might be the cleavage of pectins in spruce and formation of new COOH by the acid treatment. Pectins are esters and they can be hydrolyzed by acids leading to methanol and carboxyl groups.

3.3. Potentiometric titration

As given in the experimental section, titration of spruce wood in triplicate gave an average concentration of carboxylic acid groups of 87 µmol/g dry wood. This is similar to the result 90 µmol/g dry wood obtained by methylene blue sorption. Titration curves for torrefied wood are given in Fig. 3. The pH of the suspension is given versus the volume of added sodium hydroxide during the titration. Compared to the blank curve, the wood curve tends toward the right side, resulting from the existence of weak acids. The movement of the titration curves from right to left with increased torrefaction temperature results from less acid content in the torrefied wood. Torrefaction of wood resulted in a clear shift of the inflection point of the titration curve to the left and thus the concentration of the carboxylic acids. An explanation for this is that part of the HNO_3 added before titration is consumed in the neutralization of alkaline salts formed during torrefaction. Small irregularities in the curves are due to some delay in the stabilization of the pH in the solution containing the biomass particles.

Therefore additional torrefaction experiments with untreated wood were run at 260 and 300 °C. After torrefaction, the chars were acid washed to remove metals following the same procedure as with the acid washed wood. After acid washing, the chars were thoroughly rinsed with ultrapure water and then dried. They were then titrated as done with the other samples. This method shifted the curves to the right of the blank, resulting in a measured carboxylic acid content after torrefaction at 260 °C of 29 µmol/g as compared to 19 for acid washed wood torrefied at 260 °C, Fig. 4. This figure depicts that metals bonded organically or inorganically do not dramatically affect the destruction of carboxylic acid sites at torrefaction conditions. The acid-washed then torrefied samples and torrefied then acid-washed samples do not appear to be significantly different. However when no treatment on the samples is performed, the curves shift to the left side. This could be due to the neutralization of some of the added acid by alkaline salts and by organically bound metals in the samples.

The concentration of carboxylic acid groups as measured by potentiometric titration was 9 µmol/g for the acid washed char compared to 15 µmol/g for the acid washed wood torrefied at 300 °C, Table 3.

The concentration of carboxylic acid groups in the acid washed wood was 112 µmol/g, which is higher than that measured by methylene blue titration by about 10 µmol/g. The titration results for acid washed wood torrefied at 260 °C agree well with the methylene blue sorption results, while at 300 °C, the titration results give twice as much as the methylene blue, but the total amounts

Table 2
Mass loss and the amounts of the carboxylic groups in different torrefaction temperature for untreated wood by methylene blue sorption method.

Temperature (°C)	Raw	180	200	240	260	280	300
Mass loss (%)	0	5.5 ± 0.3	61 ± 0.7	9.8 ± 1.7	16.2 ± 2.0	22.4 ± 1.3	34.1 ± 1.1
Carboxylic acid (µmol/g wood)	90	98	93	45	22	15	3

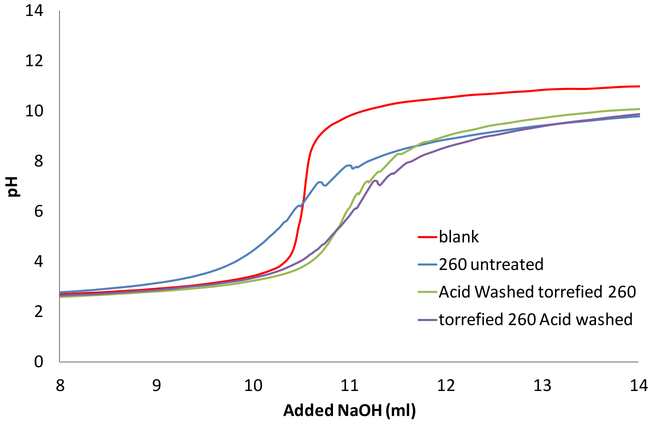

Fig. 4. Potentiometric titration curve of blank and torrefied wood at 260 °C.

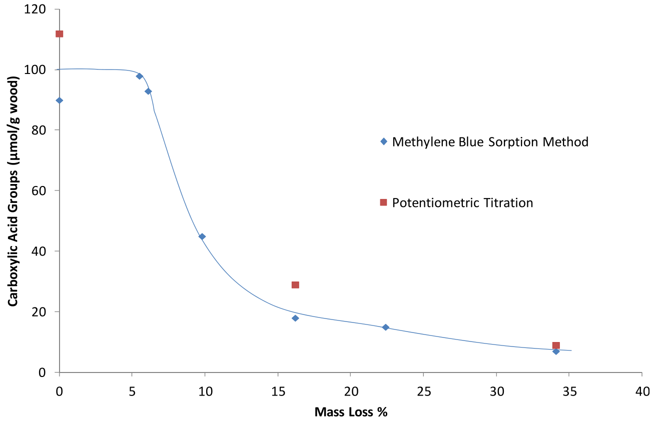

Fig. 6. Comparing the results of carboxylic groups by methylene blue sorption and potentiometric titration.

Table 3
Carboxylic acid concentration in wood and its torrefied form measured by potentiometric titration.

Original wood	87	µmol/g of original wood
Torrefaction at 260 °C	29*	µmol/g of original wood
Torrefaction at 300 °C	9*	µmol/g of original wood
Acid-washed wood	112	µmol/g of original wood
Torrefaction at 260 °C	19	µmol/g of original wood
Torrefaction at 260 °C	15	µmol/g of original wood

* Torrefied samples were acid-washed before titration.

are the lowest so the actual difference is less than the difference for the acid washed wood which has not been torrefied.

Metal ions in wood are at least partially associated with carboxylic acid sites in wood (DeGroot, 1985; Werkelin et al., 2010; Sjöström, 1989; Sundén et al., 2000). However, there appears to be no clear difference in the destruction of carboxylic groups during torrefaction of carboxylic groups in unwashed and acid washed spruce indicating that metals may not have a significant effect on torrefaction.

3.4. Equilibrium moisture content

The equilibrium moisture content (EMC) results for the torrefied wood samples are consistent with the degradation results for the carboxylic acid groups, Fig. 5. There is decreasing moisture content with increased torrefaction temperature, primary axis. This change is more clearly seen at 98% relative humidity than 75% and below. These equilibrium moisture content results are consistent with those reported elsewhere (Acharjee et al., 2011; Almeida et al., 2009). As the biomass becomes less hydrophilic, it also becomes more resistant to biological decay (Chaouch et al., 2010; Hakkou et al., 2005; Kamdem et al., 2000; Temiz et al., 2006.

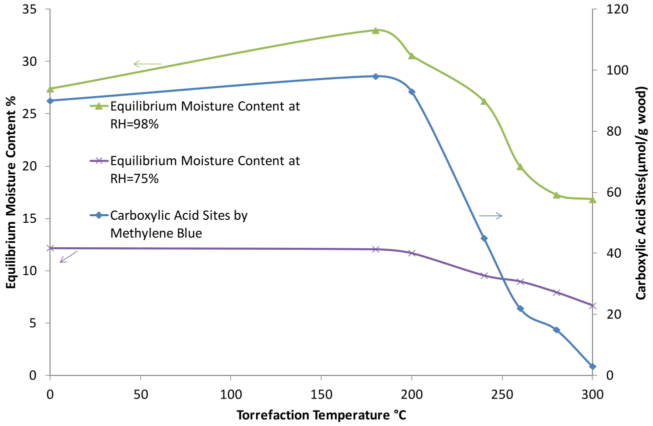

Fig. 5. Equilibrium moisture content of torrefied wood samples at different relative humidity and the comparison of its sensitivity with carboxylic acid sites versus temperature.

The decrease in the concentration of carboxylic acid groups, secondary axis, corresponds well to the decrease in the EMC at 98% relative humidity.

3.5. Comparison of results methods (potentiometric titration and methylene blue sorption)

Both methods show the same decrease in the concentration of carboxylic acid groups as the extent of torrefaction increases, Fig. 6. The concentration given by potentiometric titration was consistently higher than the value given by methylene blue sorption. Maher and Schafer (1976) measured the concentration of carboxylic groups in coal by both titration and an ion exchange method and found that titration gave a higher concentration of carboxylic acid sites. The slightly higher concentration obtained by potentiometric titration may be due to better penetration of protons into the samples.

The data in Fig. 6 shows how the extent of carboxylic acid degradation is not tied to mass loss. Most of the decrease in carboxylic acid sites occurs at a temperature of between 240 and 260 °C. Further decreases are modest and accompanied by a significant increase in mass loss. These methods can provide additional detailed information about the chemical changes during torrefaction reactions and that may help better determine what conditions give the desired results.

4. Conclusions

Both the methylene blue sorption and potentiometric titration methods were successfully applied to measure the change in carboxylic acid groups with increased torrefaction temperature. This is useful because it quantifies the degradation of carboxylic groups, which is a key reaction to the reduced hydrophilicity of the biomass. As a result, these methods can be used to help tune the torrefaction conditions.

Additional work will be carried out to determine the impact of torrefaction in different reaction times and with different biomass feedstock. Further studies are also needed on the role and fate of metals during torrefaction.

Acknowledgements

The authors wish to thank Luis Bezerra for his help in sample preparation and torrefaction, and also Jens Krogell for his help in acetone extraction of the samples. The Graduate School in Chemical Engineering is gratefully acknowledged for its support of Tooran Khazraie Shoulaifar's PhD studies.

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